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The Mineralogy of Microbiologically Influenced Corrosion

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5.1 INTRODUCTION

Microbiologically influenced corrosion (MIC) is caused by the presence and activities of microorganisms [1]. MIC is best understood as microbiologically mediated reactions with metal oxides, disruptions of passivating layers, or formation/dissolution of minerals. The following sections will review the mineralogy associated with MIC. The relationships between microbiologically mediated reactions and metal oxides define many of the mechanisms for MIC. For example, MIC can involve disruption of a passivating oxide (e.g., underdeposit corrosion), conversion of a protective oxide to a less protective layer (e.g., sulfide derivitization), or removal of an oxide layer (e.g., metal oxide reduction). Microorganisms can also produce minerals, particularly sulfides, which could not be produced abiotically in most near-surface aquatic environments. Consequently, in some cases sulfides are mineralogical indicators of MIC.

Throughout this chapter, the terms “oxide,” “passivating layer,” “mineral,” “scale,” and “corrosion product” will be used repeatedly. The terms have unique meanings and will not be used interchangeably. Upon exposure to oxygen, many metals form an oxide. In some cases, the oxide is a passive layer, i.e., a kinetic barrier at the metal–electrolyte interface that retards further metal dissolution. Not all metal oxides are passivating. For some metals, oxidation continues until all metal is converted to an oxide. The term “mineral” will be used to describe solids that are representable by a distinct chemical formula and an ordered atomic structure. Based on this definition, metal oxides are minerals with chemical formulas, while passivating layers may not be specific minerals. For example, the passivating layer on 316L stainless steel (SS) (UNS S31603) consists of a heterogeneous Cr_2O_3 (chromium oxide) film, with elemental iron, nickel, and their respective oxides, and cannot be represented with a single chemical formula. Mineral formation can be the result of either abiotic (e.g., cathodic polarization) or biotic (e.g., manganese biomineralization) reactions.

“Scale” is the precipitation product of a sparingly soluble salt that has exceeded its equilibrium solubility concentration. Most scales are minerals, e.g., MgCO_3 (magnesium carbonate) or $\text{Fe}_2(\text{CO}_3)_3$ (iron carbonate). CaCO_3 (calcium carbonate) is the most common scale mineral associated with corrosion products. “Corrosion product” is a collective term for the materials formed as a result of corrosion. There is confusion in the literature about the use of the term scale. For example, Frankel [2] used scale to describe chromium oxides on SS surfaces. In others, “scale” is used to refer to iron corrosion products [3,4]. Both are appropriate with adequate definition or explanation. However, in the following sections the term “scale” will be limited to precipitation products from the electrolyte due to either abiotic or biotic reactions.

The lists of microorganisms involved in MIC and the MIC mechanisms they control are continuously growing. Causative microorganisms are from all three main branches of evolutionary descent, i.e., bacteria, archaea (methanogens), and eukaryota (fungi). In natural environments, microbial cells attach to solids. Immobilized cells grow, reproduce, and produce extracellular polymeric substances (EPS), i.e., macromolecules such as proteins, polysaccharides, nucleic acids, and lipids. The result is a biofilm. Microorganisms within biofilms are capable of maintaining environments at the biofilm–substratum interface that are radically different from the bulk in terms of pH, dissolved oxygen, organic, and inorganic species. As a consequence, microorganisms within biofilms can produce minerals and mineral replacement reactions that are not predicted by thermodynamic arguments based on the chemistry of the bulk medium. Biofilm accumulation is the net result of attachment, growth, and detachment. Microorganisms require water, electron donors/acceptors, and nutrients for growth. The organisms known to influence corrosion are frequently grouped by electron

acceptor, energy source, or corrosive by-product linked to the resulting corrosion, e.g., sulfate- and iron-reducing; sulfur-, iron-, and manganese-oxidizing; or acid- and sulfide-producing.

Sulfate-reducing bacteria (SRB) are the organisms most commonly identified with MIC. SRB are a group of ubiquitous, diverse anaerobes, which use SO_4^{2-} (sulfate) as the terminal electron acceptor, producing hydrogen sulfide. SRB have been isolated from a variety of environments [5,6] including seawater, where the concentration of sulfate is typically 25 mM [6]. Even though the dissolved oxygen content of seawater above the thermocline ranges from 5 to 8 ppm, anaerobic microorganisms survive in anaerobic microniches until conditions are suitable for their growth [7]. If the aerobic respiration rate within a biofilm is greater than the oxygen diffusion rate, the metal–biofilm interface can become anaerobic and provide a niche for sulfide production by SRB [8,9]. The critical biofilm thickness required to produce anaerobic conditions depends on the availability of oxygen and the respiration rates of organisms in the biofilm. The metabolic activity of SRB causes accumulation of hydrogen sulfides (H_2S , HS^-) near metal surfaces.

Corrosion mechanisms attributed to SRB include the following: cathodic depolarization by the enzyme dehydrogenase, anodic depolarization, production of metal sulfides, release of exopolymers capable of binding metal ions, sulfide-induced stress corrosion cracking, and hydrogen-induced cracking or blistering. Enning et al. [10] demonstrated electron transfer between lithotrophic marine SRB and mild steel surfaces covered with a corrosion product of amorphous FeS (iron sulfide), FeCO_3 (siderite), magnesium carbonate, and calcium carbonate. They concluded that the conductivity was due to iron sulfide. The SRB used iron as an electron donor for fueling sulfate reduction. Enning et al. [10] stressed that only particular species of SRB can effectively exploit iron as an electron donor. Coleman et al. [11] identified SRB capable of Fe^{3+} reduction. Instead of reducing Fe^{3+} indirectly through the production of sulfide, these SRB reduce Fe^{3+} directly through an enzymatic mechanism, producing siderite rather than iron sulfide.

In the following sections, the mineralogy of MIC will be reviewed. Metals and alloys have been divided into active and passive categories based on the thermodynamic stability of metal/alloy oxides. Not all metals and alloys are discussed because in some cases, e.g., lead, there are no data related to MIC. The approach was to relate specific metal–microorganism reactions to mineral formation or dissolution. In some cases, minerals are the corrosion products, while in other cases, biomineralization caused the corrosion. The potential mechanisms for MIC vary markedly between the passive and active metals and alloys.

5.2 PASSIVE ALLOYS

The metals and alloys that are typically cited as having corrosion resistance due to passivation are the titanium alloys, high-alloyed steels, nickel–chromium–molybdenum alloys, and aluminum alloys. Passivity, in all cases, is limited to a range of environmental conditions. For example, under most exposure conditions, active metals such as low-alloy steel and copper alloys are not protected by a passivating layer. However, iron oxides on unalloyed steel in alkaline media (e.g., steel in concrete) are passive. Similarly, copper forms passivating layers in alkaline solutions. In all cases, if the passive layer is destroyed or disrupted, localized corrosion can occur.

5.2.1 Titanium

The corrosion resistance of titanium alloys is due to the formation of a highly stable, tenacious, adherent oxide, typically 50 to 200 Å thick. The oxide is primarily TiO_2 (titanium dioxide; highly crystalline rutile and/or its amorphous polymorph, anatase). Because titanium has a high affinity for oxygen, the oxides form spontaneously when titanium metal is exposed to oxygen. There are no reported case histories of MIC for titanium and its alloys. Schutz [12] concluded that at temperatures below 100 °C, titanium is not vulnerable to iron/sulfur-oxidizing, SRB, acid-producing bacteria (APB), differential aeration cells, chloride concentration cells, or hydrogen embrittlement.

5.2.2 Ni–Cr–Mo Alloys

Passive oxide layers on nickel–chromium–molybdenum alloys are MoO_3 (molybdenum oxide) or chromium oxide. Enos and Taylor [13] demonstrated that SRB did not cause the corrosion of welded alloy 625 (UNS N06625). No evidence of MIC in nickel–chromium and nickel–chromium–molybdenum alloys has been reported.

5.2.3 Stainless Steels

Steel alloys are categorized into two groups: low-alloy and high-alloy steels. SS contain a minimum of 10.5 wt% chromium. SS and related nickel-based high-grade alloys owe their corrosion resistance to thin-surface oxide layers. The

composition of the passive layers on SS is influenced by the alloy composition. Neville and Hodgkiess [14] assessed air-formed passive layers and passive layers that formed after a short exposure to synthetic seawater for the following SS: UNS S31603, UNS S31254, UNS S32654, and UNS S32760. Nickel was not present as an oxide or oxide/hydroxide in any of the alloys. Molybdenum (Mo) could only be detected in the passive layer of alloys containing 4% Mo or more. Superior alloys in terms of resistance to localized corrosion exhibited relatively low Fe/Cr ratios. There are no reports of MIC in SS alloys containing 6% Mo or more [1].

5.2.3.1 Groups of Microorganisms Associated with Corrosion of SS

5.2.3.1.1 Metal-Depositing Bacteria

Neville and Hodgkiess [14] reported that the poorest corrosion performance was observed with SS alloys having the highest Fe/Cr ratios in air and seawater (e.g., UNS S31603 and UNS S30400/S30403). Accordingly, there are many reports of MIC for these materials. The stability of the passive layers on these two alloys requires a uniform oxide layer. In an oxygenated environment, any deposit (biological or abiotic) that disrupts that layer causes localized corrosion (Figure 5.1). This type of corrosion is called underdeposit corrosion or crevice corrosion and results from an oxygen concentration cell, sometimes referred to as a differential aeration cell. The organisms that are most often cited as causing underdeposit corrosion are the iron- and manganese-oxidizing bacteria (FeOB and MnOB, respectively). FeOB bacteria oxidize soluble ferrous ions to insoluble ferric ions (Fe^{3+}) to obtain energy (Figure 5.2(a)). The FeOB genera that have been cited as causing MIC are neutrophilic, microaerophilic stalk- and sheath-producing, e.g., *Gallionella*, *Sphaerotilus*, *Crenothrix*, *Siderocapsa*, *Clonothrix*, *Leptothrix* [1], and *Mariprofundus* [16]. The accumulation of FeOB cells, extracellular stalks/sheaths (Figure 5.2(b)), and bacteriogenic iron oxides (BIOS) often produce dense mound-shaped deposits called tubercles (Figure 5.3). The tubercles exclude oxygen from the area immediately under the deposit and initiate a series of events that are individually or collectively very corrosive. The area under a deposit becomes a relatively small occluded anode compared with the large surrounding boldly exposed oxygenated cathode. The metal will dissolve, forming metal cations at anodic sites. If a metal hydroxide is the thermodynamically stable phase in the solution, metal ions will be hydrolyzed by water with the formation of protons. If cathodic and anodic sites are separated, the pH at the anode will decrease. Cathodic reduction of oxygen may result in an increase in pH. The pH at the anode depends on specific hydrolysis reactions determined by the metallurgy of the alloy.

In addition, if chloride (Cl^-) is present in the electrolyte, it will migrate to the anode to neutralize any buildup of charge, forming heavy metal chlorides that are extremely corrosive. Under these circumstances, underdeposit corrosion involves differential aeration, a large cathode:anode surface area, and the development of acidity and metallic chlorides. Propagation depends on metallurgy and specific hydrolysis reactions within the occluded area, not the activities of microorganisms [17]. This also means that attempts to kill the organisms within BIOS deposits using biocides will not result in a cessation of corrosion propagation [18]. Tubercle formation on 300 series SS has been investigated extensively and in most cases the formation has been attributed to FeOB without any demonstration of cells or biomineralogy.

Divalent manganese (Mn^{2+}) is soluble and the oxidized forms, Mn_2O_3 (bixbite), MnOOH (manganite), hausmannite Mn_3O_4 (hausmannite), and MnO_2 (pyrolusite), are insoluble. Tyler and Marshall [19] were among the first ones to identify stalked budding *Hyphomicrobium* as MnOB responsible for manganese deposition in freshwater pipelines. *Hyphomicrobium* cells are negatively charged with carboxylic groups on their surfaces. The budding mode of reproduction accounts for their reproductive efficiency and their ability to coexist with the manganese oxides they reproduce. Microbially deposited manganese oxides are $(\text{Mn}^{4+}, \text{Fe}^{3+}, \text{Ca}, \text{Na})(\text{O}, \text{OH})_2 \cdot n(\text{H}_2\text{O})$ (vernadite) and MnO_2 (birnessite) [20]. Birnessite

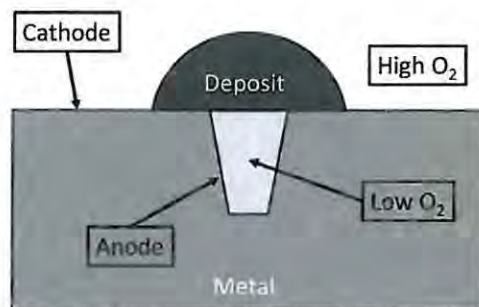


FIGURE 5.1 Schematic of differential aeration cell.

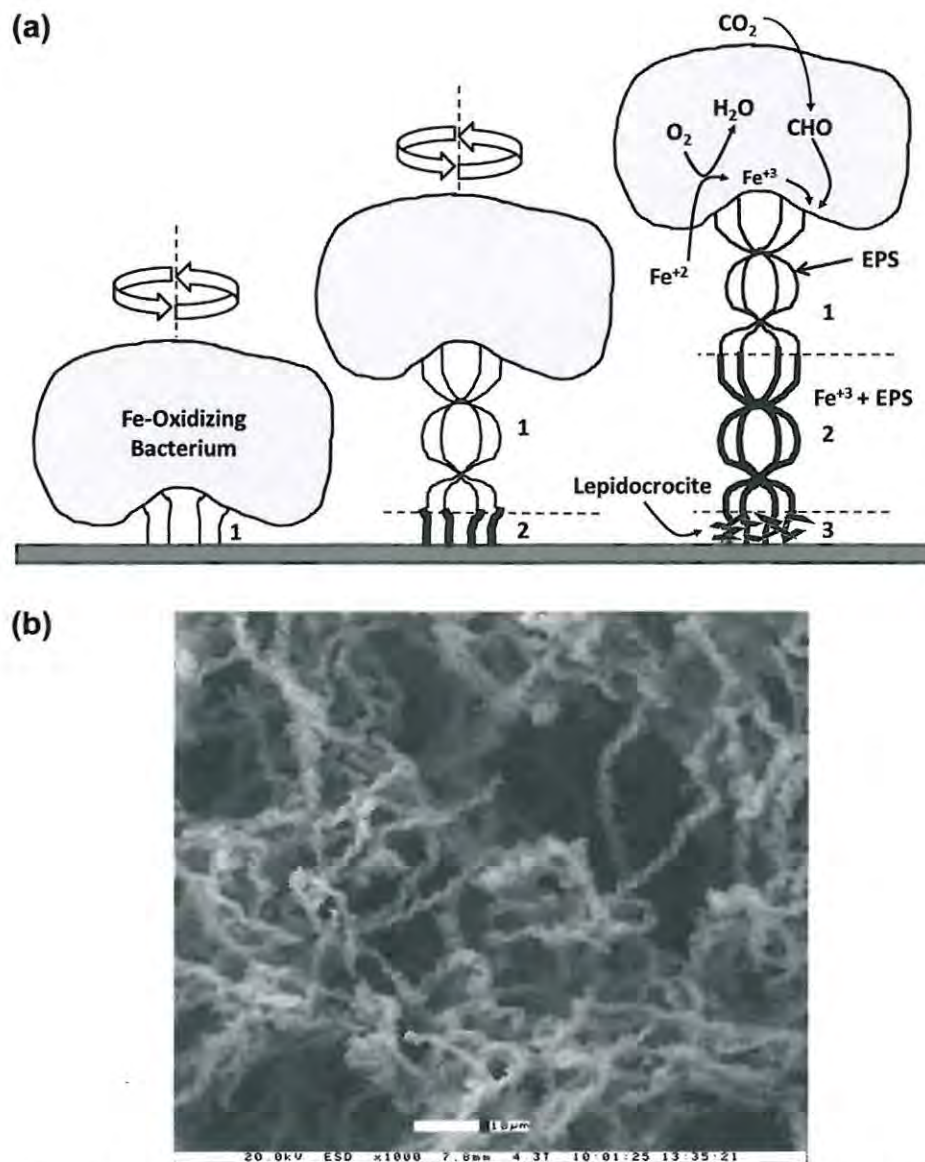


FIGURE 5.2 (a) Model of stalk formation and biomineralization process. Fe^{2+} oxidation is coupled to O_2 reduction within the cell, the exact location is unknown. (1) Extracellular polymeric substances are excreted from cells as fibrils. As the cell rotates, twisted stalks are produced. (2) Over time, Fe^{3+} precipitates as Fe oxyhydroxides, collectively termed as bacteriogenic iron oxides. (3) As stalks age, lepidocrocite nucleates on fibril surfaces. (Adapted from Chan *et al.* [15].) (b) Twisted stalks of iron-oxidizing bacteria encrusted with iron oxides.

can recrystallize to octahedral Mn_3O_4 [21]. Anodic corrosion currents allow biomineralized manganese oxides to accumulate. Open-circuit potential, also known as corrosion potential (E_{corr}), then shifts in the noble direction (ennoblement) as increasing areal coverage anodically polarizes the metal. E_{corr} may reach the pitting potential for low-molybdenum alloys in dilute chloride media, increasing the risk of pit nucleation. Once nucleation occurs, cathodic current sustained by the birnessite cathode impedes repassivation by holding the corrosion potential above the protection potential [22]. Manganic (Mn^{3+}) oxides are efficient cathodes and increase cathodic current density on SS by several decades at potentials (vs saturated calomel electrode (SCE)) between roughly -200 and $+400$ mV(SCE). More cathode material (manganic oxide) will support a greater number of pitting sites, increasing the probability that a metastable site will become fixed. The extent to which the elevated current density can be maintained is controlled by the electrical capacity of the mineral–biopolymer assemblage (only material in electrical contact with the metal will be cathodically active). The biomineralization rate and the corrosion current control oxide accumulation. Localized corrosion current that exceeds the biomineralization rate will discharge the oxide cathode, so that eventually the



FIGURE 5.3 Tubercles on stainless steel.

corrosion rate becomes limited by the oxide biomineralization rate and by availability of other cathodic reactants (typically, dissolved oxygen). High corrosion currents discharge the oxide as rapidly as it is formed [23].

5.2.3.1.2 Sulfate-Reducing Bacteria

Literature describing the effect of SRB on the corrosion of SS is contradictory. McNeil and Odom [24] developed a thermodynamic model for predicting SRB-influenced corrosion based on the likelihood that a metal oxide would react with microbiologically produced sulfide to produce a metal sulfide (derivitization). The model is based on the assumption that SRB-induced corrosion is initiated by sulfide-rich reducing conditions in a biofilm and that under those conditions, the metal oxide is destabilized and acts as a source of metal ions. If the reaction to convert the metal oxide to a metal sulfide has a positive Gibbs free energy under surface conditions, the sulfides will not strip the oxide and no corrosion will take place. If the Gibbs free energy for that reaction is negative, the reaction will proceed. The model predicts that metal oxides on SS containing 6% or more Mo will be very resistant to derivitization by sulfides and that reaction rates for all SS will be slower than those for pure iron or low-alloy steel.

Webster and Newman [25], working with a creviced SS (Fe–15Cr–10Ni), reported that the composition of the electrolyte influenced SRB corrosion, especially the ratio of aggressive anions (i.e., Cl^-) to inhibiting anions (e.g., nitrate, sulfate, phosphate). Localized corrosion would not readily occur unless Cl^- was the predominant anion in the medium. They concluded that the Cl^- concentration must be at least comparable to the concentration of the sum of all the other anions in the medium, otherwise corrosion was inhibited even at H_2S concentrations up to 500 ppm. Reduction of the ratio of Cl^- to inhibiting anions increased the time to initiation and decreased the rate of propagation of the corrosion. In their experiments, a specially designed medium, a crevice assembly, and an oxygen-reduction cathode were required to produce corrosion of Fe–15Cr–10Ni with SRB.

Neville and Hodgkiess [26] conducted laboratory experiments that demonstrated that SRB could disrupt the passive behavior of a range of SS (UNS S31803, UNS S32760, and UNS S31603) both under “free corrosion conditions and under the influence of modest anodic polarization” in seawater. Their work also demonstrated the important role of molybdenum and chromium in conferring resistance to passive film breakdown in seawater with SRB.

$\text{S}_2\text{O}_3^{2-}$ (thiosulfate) and sulfur are potential oxidation products of HS^- produced by SRB. Thiosulfate can induce pitting on UNS S30403 at relatively negative electrode potentials in the absence of Cl^- [27]. Adsorbed sulfur species can catalyze anodic dissolution and hinder passivation in pits and crevices.

5.2.4 Aluminum and Aluminum Alloys

The corrosion resistance of aluminum and its alloys is due to an aluminum oxide passive film. Anodizing produces thicker insulating films and better corrosion resistance. The natural film on aluminum alloys can be attacked locally by halide ions. The susceptibility of aluminum alloys to localized corrosion makes them particularly vulnerable to MIC [28].

5.2.4.1 Groups of Microorganisms

5.2.4.1.1 Acid-Producing Bacteria and Fungi

Most reports of MIC are for aluminum (99%), 2024 (UNS A92024), and 7075 (UNS A97075) alloys used in aircraft or in underground fuel storage tanks [29]. Localized corrosion attributed to MIC occurs in the water phase and at the fuel–water interface. Soluble fuel components, contaminants, and additives determine the extent and type of microbial growth [30]. The most frequently cited mechanism for MIC of aluminum alloys is microbial production of water-soluble organic acids by bacteria and fungi. Fungal mycelia can produce acid-etched trenches in some alloys (Figure 5.4).

5.2.4.1.2 Sulfate-Reducing Bacteria

McNeil and Odom [24] indicated that there were no thermodynamic data for the conversion of aluminum oxides to sulfides. Characterization of aluminum sulfides is complicated because most are soluble and dissolve as they form. However, investigators have demonstrated pitting of alloys 7075 and 2024 exposed to SRB [31].

5.3 ACTIVE METALS

Active metals form nonprotective, porous oxide layers. These oxide layers of active metals can flake off, allowing continued corrosion or they can be dissolved or derivitized [24]. The McNeil–Odom model predicts that active metals will be derivitized by microbiologically produced sulfides. The prediction is limited to thermodynamic predictions as to whether or not a reaction will take place and does not consider metal toxicity to organisms, tenacity of the resulting sulfide, or other factors that influence corrosion rate.

5.3.1 Iron and Low-Alloy Steel

There are several categories of low-alloy steel. The main alloying element in carbon steel is carbon (C) and the mechanical properties of the carbon steel depend on the percentage of carbon. Low-carbon steel contains approximately 0.05–0.3% C and mild steel, 0.3–0.6% C. Alloys with a higher than 2.1% C (depending on other element content and possibly on processing) are cast irons. Ductile iron contains nodular graphite (C) inclusions that contribute to impact and fatigue resistance. The oxide, typically referred to as rust, that forms on these materials is Fe_2O_3 (hematite). Upon exposure to moisture, α - FeOOH (goethite), β - FeOOH (akaganeite), γ - FeOOH (lepidocrocite) and Fe_3O_4 (magnetite) are formed. Stratmann and Muller [32] showed that in the presence of rust layers, oxygen is reduced within the scale and not at the metal–electrolyte boundary. They demonstrated that as rust layers were reduced, magnetite was formed.

Ray et al. [33] examined the structure and mineralogy of tubercles on low-alloy steels from different freshwater sources. They concluded that the size, mineralogy, and morphology of tubercles, i.e., mounds of iron corrosion products, on carbon steel and cast iron surfaces from treated and untreated waters were remarkably similar, suggesting that formation was controlled by something other than water quality and microorganisms. Tubercles on low-alloy steels were made up of a surface layer, shell, and core with the same general distribution of iron minerals (Figure 5.5). In all cases, the outermost surface layer and the innermost core contained Fe^{3+} minerals (goethite; $\text{Fe}^{3+}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ (ferrihydrite))

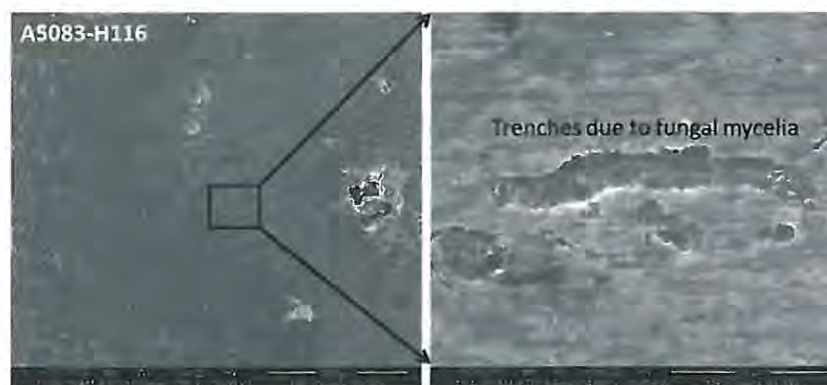


FIGURE 5.4 Fungal attack of Al–Mg alloy (UNS A5083-H116).

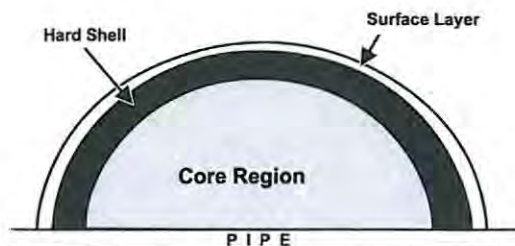


FIGURE 5.5 Schematic of tubercle on a pipe surface exposed to drinking water. (Adapted from Gerke et al. [34].) Surface layer and core region contain Fe^{3+} minerals goethite and ferrihydrite). Hard shell is magnetite, a mixed-valence mineral.

separated by magnetite. In some cases, the tubercles were associated with localized corrosion immediately underneath the accumulation of corrosion products, and in other cases, there were no indications of localized corrosion.

Gerke et al. [35] examined corrosion products with differing morphologies, e.g., mounds, mounds with protruding tubes, and freestanding tubes, on cast iron pipes that had been exposed to chlorine-disinfected drinking water (Figure 5.6). Internal morphologies for all shapes were texturally complex, although mineralogically simple, composed primarily of two iron oxide/oxyhydroxides minerals, i.e., goethite and magnetite, and minor to trace amounts of lepidocrocite. In summary, they proposed that in cast iron pipes exposed to aerated, chlorinated drinking water, metallic iron was oxidized to Fe^{2+} by dissolved oxygen in the water, released into the water, and further oxidized to Fe^{3+} , forming $\text{Fe}(\text{OH})_3$, which accumulated on the inner wall of the cast iron pipe at locations that were not necessarily associated with localized corrosion. The $\text{Fe}(\text{OH})_3$ dehydrated, producing goethite and lepidocrocite. Below a critical O_2 concentration, portions of goethite and lepidocrocite were reduced to magnetite. Gas production at the cathode caused breaks (vents) in the crust. They concluded that growth of the vents into tubes was the result of templating iron particulates on the cathodically produced gas bubbles.

5.3.1.1 Groups of Microorganisms

5.3.1.1.1 Iron- and Manganese-Oxidizing Bacteria

The works of Ray et al. [36] and Gerke et al. [35] suggested that the mineralogy of accumulated corrosion products on low-alloy carbon steels and cast iron was independent of microbially mediated reactions. Ray and coworkers [36,37] imaged iron-encrusted stalks of FeOB in the core region of some, but not all, tubercles from freshwater exposures. More recently, Lee et al. [38] demonstrated that neutrophilic, microaerophilic FeOB grew and proliferated on corroding carbon steel submerged in oxygenated marine media. Corrosion reactions reduced the dissolved oxygen concentration on the surface [39], creating conditions amenable to FeOB growth. Similarly, McBeth et al. [16] and Dang et al. [40] reported that FeOB (*Mariprofundus*) were among the first colonizers when carbon steel was submerged in a coastal seawater. The dominant mineral phase in BIOS from both fresh and marine waters is typically 2-line ferrihydrite [41,42]. Ferrihydrite is a poorly ordered mineral that transforms into goethite and/or hematite over time.

For mild steel corrosion under anodic control, manganese oxides elevate corrosion current, but will cause little positive shift in E_{corr} . The increase in corrosion current may be significant, particularly for mild steel covered with biomineralized oxides that provide large mineral surface areas. Continued biomineralization may sustain a significant amount of cathodic current.

5.3.1.1.2 Metal-Reducing Bacteria

Dissimilatory iron and/or manganese reduction occurs in several microorganisms. Inhibitor and competition experiments suggest that Mn^{4+} and Fe^{3+} are efficient electron acceptors similar to nitrate in redox ability and are capable of out-competing electron acceptors of lower potential such as sulfate or carbon dioxide [43]. Many of the recently described metal-reducing bacteria are capable of using a variety of electron acceptors, including nitrate and oxygen [43]. Iron-reducing bacteria (FeRB) derive energy from the reduction of Fe^{3+} in one of two ways: using an electron transport chain in anaerobic respiration or using Fe^{3+} as an electron sink during fermentation. FeRB can be either strict anaerobes (examples include members of the *Geobacteraceae*) or facultative anaerobes that use oxygen, but can switch to using Fe^{3+} as a terminal electron acceptor under anaerobiosis (examples include members of the genus *Shewanella*). Coleman et al. [11] demonstrated that some SRB can reduce Fe^{3+} .

A relationship between microbial manganese reduction and corrosion has not been established and the relationship between FeRB and corrosion is complicated. FeRB enhance corrosion under some circumstances [44] and have a

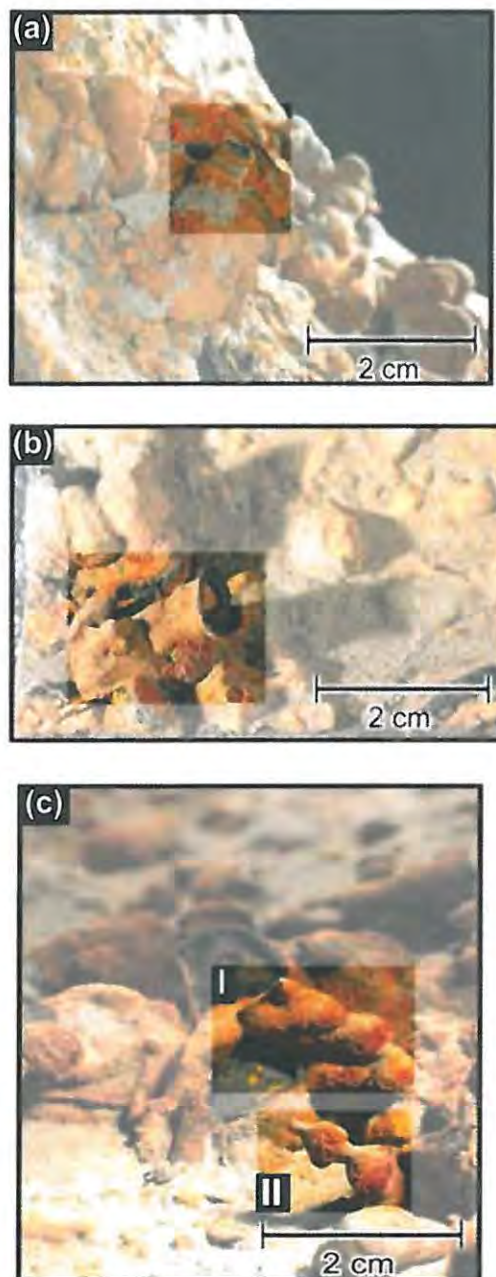


FIGURE 5.6 Digital images of representative external morphologies of representative tube-shaped iron corrosion products (a)–(c). Gerke *et al.* (2012), © NACE International [35].

passivating effect under others [44,45]. Some of the reported differences can be attributed to differences in microbial species and differences in electrolyte composition in experiments with the same organism [46]. In addition, there is variation in Fe-oxide reactivity. Using synthetic Fe-oxides (three different ferrihydrites, five lepidocrocites, and a poorly crystalline goethite) and 10 mM ascorbic acid at pH 3, Larsen and Postma [47] studied the kinetics of bulk reductive dissolution. They concluded that the relationship between mass and surface area of crystals, crystal size distribution, the relative site density, and preferential dissolution along crystalline boundaries influenced rates of dissolution. Similarly, Little *et al.* [44] demonstrated that reduction rates varied among Fe-oxides exposed to the FeRB *Shewanella putrefaciens*. Dissolution rates, measured by atomic absorption, were slower for hematite compared with the reduction rates for goethite and ferrihydrite under identical exposure conditions. It is well established that BIOS are more readily reduced by bacteria (e.g., FeRB and SRB) in comparison with synthetic iron oxides [41,48,49].

Several investigators have demonstrated both FeOB and FeRB in corrosion products [40]. The presence of FeOB-generated stalks and BIOS in biofilms provides a reactive mineral structure that can support the growth of FeRB. Microbiological iron cycling mediated by associated populations of FeOB and FeRB that carry out oxidative and reductive pathways, respectively, is a recognized phenomenon and has been studied most extensively in freshwater habitats [48,50–53]. Blothe and Roden [48] suggested that in high-iron environments, “Such recycling is likely to take place in virtually all redox interfacial environments...” FeOB and FeOB/FeRB biofilms forming at corrosion surfaces may provide anaerobic niches for microbial reduction processes such as dissimilatory Fe reduction and sulfate reduction, even in environments where the bulk conditions are oxidic [38].

5.3.1.1.3 Sulfate-Reducing Bacteria

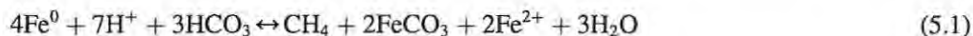
McNeil et al. [54] evaluated corrosion product mineralogy using X-ray diffraction data, thermodynamic stability diagrams (Pourbaix), and the simplicity principle for precipitation reactions. They concluded that many sulfides under near-surface natural environmental conditions could only be produced by microbiological action on specific precursor metals. They reported that tetragonal FeS_{1-x} (mackinawite) was produced by SRB from iron and iron oxides. The presence of mackinawite in corrosion products formed in shallow-water environments (with some exclusions, e.g., industrial water) is proof that the corrosion was SRB-induced.

If Fe^{2+} ion concentration in the electrolyte is low, mackinawite alters to $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{S}_4$ (greigite). This alteration is not observed in nonbiological systems. When Fe^{2+} ion concentration is high, mackinawite is accompanied by green rust 2 [$\text{GR2}(\text{SO}_4^{2-})$], a complex ferrosiferrous oxyhydroxide. Zegeye et al. [55] demonstrated that sulfate anions in green rust 2, formed during the marine corrosion of iron, were available for SRB anaerobic respiration. Green rust 1 [$\text{GR1}(\text{CO}_3^{2-})$], $\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$ (vivianite), and an iron sulfur compound were formed. On continued exposure to SRB, mackinawite alters to greigite, Fe_9S_{11} (smythite), and to FeS_{1+x} (pyrrhotite, a polymorph of mackinawite) [56]. Pyrite FeS_2 (pyrite) is not a typical iron corrosion product, but SRB can produce pyrite from mackinawite in contact with elemental sulfur [57]. Abiotic aqueous synthesis of these minerals, with the possible exception of pyrite, requires H_2S pressures higher than those found in shallow waters. Direct electron transfer from Fe^0 (zero-valent iron) by SRB in the absence of organic carbon, a typical electron donor has been documented by Enning et al. [10]. Sulfides on the surface mediated electron flow from the metal to the SRB.

Hamilton [58] recognized that sulfide minerals could undergo oxidation with the introduction of oxygen, causing corrosion rates to increase dramatically. He reviewed the literature on anaerobic corrosion of carbon steel by SRB and concluded that oxygen was required for aggressive SRB-influenced corrosion. He summarized his conclusions as follows: SRB-influenced corrosion of mild steel occurs by a process of electron transfer from base metal to oxygen as the ultimate electron acceptor through a series of coupled redox reactions of, respectively, electrochemical, biotic, and abiotic character. The microbial activity at a metal surface resulted in a kinetically favored pathway of electron flow, giving rise to increased oxidation (corrosion weight loss) of iron. He concluded that all microbial mechanisms, both aerobic and anaerobic, involved a process of electron transfers from base metal to oxygen as the ultimate electron acceptor through a series of coupled reactions. He hypothesized that in the case of SRB and carbon steel, sulfate, an intermediate electron acceptor, is reduced to sulfide that reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. In the model, sulfate is the terminal electron acceptor in anaerobic respiration, but oxygen is the terminal electron acceptor in the corrosion reaction. In his model, he hypothesized that microbial activity generates appropriate products and kinetically favored pathways for electron flow from the metal anode to the universal electron acceptor, oxygen. Hamilton [58] reviewed the data of others [59,60] in developing his hypothesis and in most cases experiments were conducted under alternating anaerobic and aerobic conditions. The relationship between SRB-influenced corrosion and oxygen however is more complicated than sequential shifts in dissolved oxygen concentrations (anaerobic followed by aerobic). Aktas et al. [61] demonstrated that low levels of oxygen (<100 ppb) in natural seawater influenced biodegradation pathways for alternative plant-derived fuels and subsequent SRB-influenced corrosion of carbon steel.

5.3.1.1.4 Methanogens

Methanogens, archaea capable of growth on molecular hydrogen (H_2) and CO_2 , are often found in biofilms with H_2 -consuming SRB at corrosion sites. Direct uptake of electrons by methanogens from iron has also been demonstrated as a mechanism for corrosion. Park et al. [62] identified siderite as a corrosion product consistent with microbial methanogenesis:



5.3.1.1.5 Acid-Producing Bacteria

There is little difference in the corrosion rate of low-alloy steels in natural fresh, tap, and distilled water with pH values between 4.5 and 9.5. In this range, the corrosion products maintain a pH of 9.5 next to the steel surface independent of the pH of the solution [63]. APB are recognized as a major cause of corrosion of low-alloy steels, mainly because their fermentative activities will cause the pH, particularly in the biofilms, to drop into the acid range at the metal surface. Under these conditions, an acid-driven form of corrosion could occur, where the metal oxides dissolve. The kinds and amounts of acids produced depend on the type of microorganisms and the available substrate molecules. Organic acids may force a shift in the tendency for corrosion to occur. The impact of acidic metabolites is intensified when they are trapped at the biofilm–metal interface. In addition, it has been demonstrated that the organic acids of the Krebs cycle can promote the electrochemical oxidation of a variety of metals by removing or preventing the formation of an oxide film.

Elemental sulfur, thiosulfates, metal sulfides, H_2S , and tetrathionates can be oxidized to sulfuric acid by microorganisms generically referred to as thiobacilli, sulfur-oxidizing bacteria. A sulfur cycle that includes SRB and thiobacilli is reportedly responsible for the aggressive corrosion of low-alloy steel pilings in marine and estuarine ports around the world [64]. The phenomenon is called accelerated low-water corrosion because the precise location of the localized corrosion (pitting) is directly related to aerobic and anaerobic niches produced during the tidal cycle.

5.3.1.2 Cathodic Protection

Low-alloy steels are rarely used in corrosive environments without some corrosion protection, e.g., coatings or cathodic protection (CP). CP is a technique used to control the corrosion of a metal surface, particularly low-alloy steel in marine environments, by making it the cathode of an electrochemical cell. CP can be achieved by connecting the metal to be protected to a more easily corroded “sacrificial metal” to act as the anode (galvanic CP). The sacrificial metal then corrodes instead of the protected metal. For structures such as long pipelines, where galvanic CP is not adequate, an external DC electrical power source (impressed current CP) is used to provide a cathodic current. Mineral scales of CaCO_3 (aragonite) and $\text{Mg}(\text{OH})_2$ (brucite) develop on cathodically protected steel surfaces immersed in seawater. Impressed current CP forces the following reactions:



The increase in alkalinity shifts the equilibrium to the following reactions, where hydroxyl ions cause the precipitation of magnesium hydroxide if the surface pH is 9.3 or higher:



The kinetics of mineral formation depends on temperature, applied potential, hydrodynamics, and seawater composition. When referring to the characterization of calcareous deposits, Barchiche et al. [65] state, “If the main trends are clearly established, numerous contradictory results and conclusions remain.”

NACE Standard SP0169-2007 [66] lists CP criteria for underground or submerged steel, cast iron, and ductile iron. Paragraph 6.2.2.1.1 specifies that for steel and cast iron piping, “A negative (cathodic) potential of at least 850 mV with the CP applied. This potential is measured with respect to a saturated copper/copper sulfate reference electrode contacting the electrolyte.” Bacteria are mentioned throughout the standard. In paragraph 1.4, there is a list of special conditions in which CP is ineffective or only partially effective. “Such conditions may include elevated temperatures, disbonded coatings, thermal insulating coatings, shielding, bacterial attack, and unusual contaminants in the electrolyte.” Paragraph 7.1.2.6 states, “Special consideration should be given to the presence of sulfides, bacteria, disbonded coatings, thermal insulating coatings, elevated temperatures, shielding, acid environments, and dissimilar metals.” Paragraph 6.2.2.2.2 indicates, “In some situations, such as the presence of sulfides, bacteria, elevated temperatures, acid environments, and dissimilar metals, the criteria in Paragraph 6.2.2.1 may not be sufficient.” Horvath and Novak [67] studied thermodynamic data with iron in a pH-7 electrolyte saturated with hydrogen sulfide. A potential of $-1024 \text{ mV}_{(\text{SCE})}$ was required to achieve CP. Carbon steel is considered protected when a potential of $-924 \text{ mV}_{(\text{SCE})}$ is achieved. In many cases, the potential is further reduced to

$-1024 \text{ mV}_{(\text{SCE})}$ to protect the steel from corrosion caused from the activity of SRB. The decreased potential is not applied to prevent the growth of SRB, but is based on a theoretical level which will allow passivity of steel in a sulfide-rich environment produced by SRB.

Microbiological data from cathodically polarized surfaces are contradictory. For example, it has been reported that CP retards microbial growth because of the alkaline pH generated at the surface. However, numerous investigators have demonstrated a relationship between marine fouling and calcareous deposits on cathodically protected surfaces [68–73].

The influence of CP on the growth of SRB and on the corrosion of steel in marine sediments was investigated by Guezennec and Therene [74]. They concluded that a cathodic potential of $-880 \text{ mV}_{(\text{SCE})}$ did not appear to be sufficient for protection and that large amounts of cathodically produced hydrogen promoted the growth of SRB in the sediments surrounding the samples. Fischer [75] conducted laboratory tests in anaerobic, artificial sediments containing SRB. Results indicated that the criterion of $-1024 \text{ mV}_{(\text{SCE})}$ for protection was adequate. CP current density was between 4.5 and 12 mA/ft^2 . Barlo and Berry [76] concluded that a cathodic polarization shift of approximately -200 to $-300 \text{ mV}_{(\text{SCE})}$ was required to protect carbon steel in the presence of sulfide production by SRB. Ulanovskii and Ledenev [77] imposed CP on steel surfaces actively corroding in cultures of SRB and concluded that CP decreased corrosion by a factor of eight or nine compared with the same system without CP.

In summary, bacteria are located on cathodically protected surfaces. Cathodic potentials to $-1024 \text{ mV}_{(\text{SCE})}$ do not prevent biofilm formation. It has been suggested that actual cell numbers may be related to polarization potential, dissolved organic carbon, or enumeration technique. Numbers of SRB may be increased or decreased depending on exposure conditions. The main consequence of biofilm formation on protected surfaces appears to be an increase in the current density necessary to polarize the metal to the protected potential. The presence of large numbers of SRB on cathodically protected surfaces does mean that in the event that CP is intermittent, discontinuous, or discontinued, the corrosion attack due to the microorganisms can be aggressive.

5.3.2 Copper and Nickel

Cu_2O (cuprite), the first product of copper corrosion in oxygenated liquid media, forms epitaxially as a direct reaction product of copper with dissolved O_2 or with water molecules [78]. Cuprite has a high electrical conductivity and permits transport of copper ions through the oxide layer so they can dissolve in the water and reprecipitate. Webster et al. [79] suggested that microbial acceleration of copper corrosion in potable water was due to the incorporation of EPS into the copper oxide at the metal surface. The result was disruption of the surface oxides. If the water chemistry approximates that of seawater, copper ions reprecipitate as $\text{Cu}_2(\text{OH})_3\text{Cl}$ (botallackite) [80], which can alter in minutes or hours to either paratacamite or atacamite (polymorphs of botallackite) depending on local water chemistry.

In general, the corrosion resistance of Cu–Ni alloys increases with increasing nickel content. Uhlig and Revie [81] calculated that a critical nickel concentration of 35% was required for passivity. Copper–nickel alloys containing nickel less than this amount behave like copper. Under alkaline conditions, Cu–Ni alloys are covered by passive oxide films containing Cu and Ni oxides. In alkaline, chloride ion-containing environments, the Cu–Ni alloys are susceptible to localized corrosion because of the breakdown of the oxide layer caused by chloride ions, as chloride ions are incorporated into the oxide.

5.3.2.1 Groups of Microorganisms

Differential aeration, selective leaching, underdeposit corrosion, and cathodic depolarization have been reported as mechanisms for MIC of copper alloys. Pope et al. [82] proposed that the following microbial products accelerated localized attack: CO_2 , H_2S , NH_3 , organic, and inorganic acids; metabolites that act as depolarizers; and sulfur compounds such as mercaptans, sulfides, and disulfides.

5.3.2.1.1 Sulfate-Reducing Bacteria

Copper oxides are readily converted to copper sulfides [83]. Biomineralogy of copper sulfides has been studied for over a century [84–91]. Detailed kinetics of individual reactions is not fully understood, and the consequences for corrosion depend on many factors, including mineral morphology and variations of redox and pH with time [83]. The general phenomenology can be understood by the following approach. Microbial consortia that include SRB produce anoxic, sulfide-rich environments in which the conversion of copper to copper sulfides is thermodynamically favored at a concentration of 10^{-2} M total sulfur.

Reactions appear to proceed as suggested by Ostwald's rule: the first sulfur-poor compounds are converted to sulfur-rich compounds. One would expect a layering effect with CuS (covellite) on the outside and Cu₂S (chalcocite) next to unreacted copper metal. In short-term experiments with excess of copper over available sulfur, chalcocite with little or no covellite is formed [92]. Covellite is produced if excess sulfide is available, either deliberately provided [86] or naturally available [84,87]. Chalcocite, Cu₉S₅ (digenite), Cu₃₁S₁₆ (djurleite), Cu₇S₄ (anilite), Cu₃₉S₂₈ (spionkopite), Cu₈S₅ (geerite), and covellite have been reported. In long-term corrosion where waters contain significant iron, CuFeS₂ (chalcopyrite) is a common product [83]. While chalcopyrite films can be formed abiotically in high sulfur concentrations [93], chalcopyrite and most other copper sulfides are not generally found as products of abiotic corrosion. Djurleite, spionkopite, and the high-temperature polymorph of chalcocite were identified as mineralogical fingerprints for the SRB-induced corrosion of copper–nickel alloys.

It has been argued that if the copper sulfide layer were djurleite, the sulfide layer would be protective [94]. Even if such a sulfide film were technically passivating, the mechanical stability of the film is so poor that sulfide films are useless for corrosion protection. In the presence of turbulence, the loosely adherent sulfide film is removed, exposing a fresh copper surface to react with sulfide ions. For these reasons, turbulence-induced corrosion and sulfide attack of copper alloys cannot easily be decoupled. In the presence of oxygen, the possible corrosion reactions in a copper sulfide system are extremely complex because of the large number of stable copper sulfides [95], their differing electrical conductivities, and catalytic effects. Transformations between sulfides or of sulfides to oxides result in changes in volume that weaken the attachment scale and oxide subscale, leading to spalling. Bared areas repassivate, forming Cu₂O. Selective dealloying of zinc, nickel, and iron from copper alloys has been reported by several investigators. Little et al. [96] demonstrated dealloying of nickel from a 90/10 copper/nickel alloy in association with SRB. Nickel–copper and low-nickel alloys are also susceptible to MIC. For example, Monel 400 is susceptible to pitting and crevice corrosion attack where chlorides penetrate the passive film. Sulfides can cause either a modification or breakdown of the oxide layer. SRB produce millerite (NiS) from nickel ions, but nickel sulfides are rarely found in corrosion products [24].

Gouda et al. [97] demonstrated pitting of Monel 400 tubes exposed in Arabian Gulf seawater, where pits developed under the deposits of SRB and nickel were selectively dealloyed. Little et al. [96] reported selective dealloying in Monel 400 in the presence of SRB from an estuarine environment. Pope [98] reported a case study from nuclear power plants in which severe pitting corrosion associated with dealloying was observed under discrete deposits on Monel 400 heat exchanger tubes. Deposits formed by iron- and manganese-depositing bacteria in association with SRB contained large amounts of iron and copper, significant amounts of manganese and silicon, and reduced amounts of nickel.

5.3.2.1.2 Other Microorganisms

SRB are not necessary for MIC-induced pitting of copper alloys. While the role of the biofilm in copper pitting is not entirely clear, it appears that the presence of the biofilm contributes to corrosion by maintaining enhanced local chloride concentrations and differential aeration cells [99]. Pope [98] documented MIC of 90/10 copper/nickel tubes, admiralty and aluminum brass, and welded aluminum bronze at electric-generating facilities using fresh or brackish cooling waters. Most of the copper/nickel tubes had underdeposit corrosion due to formation of deposits by slime-forming organisms in association with iron- and manganese-depositing bacteria. Ammonia-producing bacteria were isolated from scale and organic material on the admiralty brass tubes suffering ammonia-induced stress corrosion cracking.

5.4 CASE STUDIES

Few investigators have attempted to use mineralogy of corrosion products to diagnose MIC and to provide insight into the causative microorganisms and the conditions under which the corrosion took place. For example, Jack et al. [100] examined the mineralogy of corrosion products on gas transmission pipelines (Figure 5.7). Under anaerobic conditions in the absence of SRB, siderite was identified in water trapped underneath defective coatings. Introduction of air caused a rapid discoloration of the white corrosion product to orange Fe³⁺ oxides. In the presence of SRB, siderite and Fe²⁺ sulfide were identified in a ratio of 3:1 or more. Mackinawite, the first-formed crystalline sulfide, converted to greigite in a time- and pH-dependent manner that was used to determine formation conditions, including time to formation. Jack et al. [100] reported Fe³⁺ oxides, e.g., magnetite, hematite, lepidocrocite, and goethite at aerobic sites (Figure 5.8).

McNeil and Little [91] outlined procedures for evaluating the possibility of SRB associated with copper and silver artifacts recovered from shallow land or water burial. They [91,101] used stability diagrams, i.e., two-dimensional presentations of phase equilibria controlled by two independent variables (i.e., pH and potential (E_h)), to examine corrosion product mineralogy. For example, they concluded that formation of Ag₂S (argentite) on silver-containing objects was limited to precipitation of silver ions by reduced sulfur species in the presence of copper, e.g., coins and jewelry that contained copper.

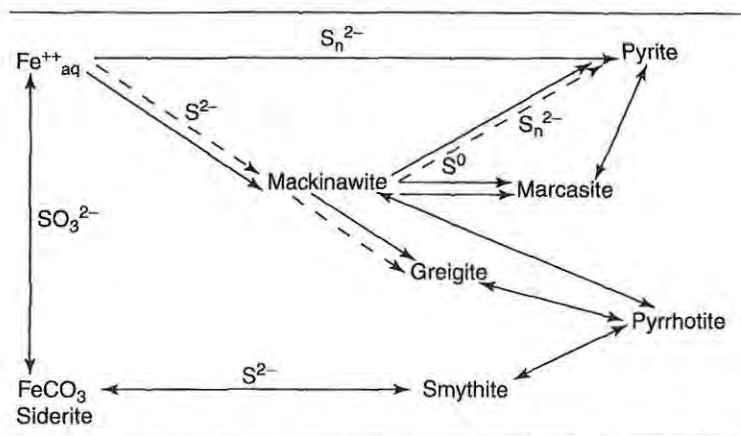
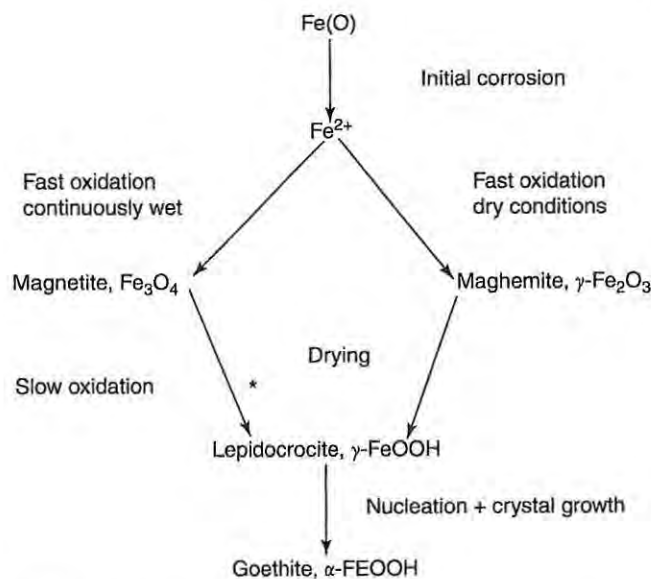


FIGURE 5.7 Transformation of Fe^{2+} sulfides formed at pipeline corrosion sites (dashes, biological processes; solid line, abiotic processes). Jack *et al.* (2012), © NACE International [100].



* Hematite may form from magnetite as an intermediate.

FIGURE 5.8 Transformation of Fe^{3+} oxides formed at pipeline corrosion sites. Jack *et al.* (2012), © NACE International [100].

5.5 SUMMARY

The relationship between minerals and MIC is both obvious and complicated. The thermodynamics of mineral formation can be used to predict the likelihood that a metal oxide will be derivitized to a sulfide in the presence of SRB. However, microorganisms can produce minerals that cannot be predicted. Both SRB and FeRB can use MIC products as electron acceptors, creating the possibility of metal cycling and chain reactions that are microbiologically mediated in corrosion products. In all cases, the mineralogy of MIC depends on the microorganism, the nature of the substratum, and the environment.

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